OFFICE OF NAVAL RESEARCH

Grant N00014-93-1-0351

R & T Code 96PRO-5486

Technical Report No. 25

# Studies of the Electrochemical Double Layer at Au(100) in Perchloric Acid Solutions by In Situ Infrared Spectroscopy

by

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Prepared for Publication

in

Journal of the Electrochemical Society

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May 26, 1996

# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
5/26/96

3. REPORT TYPE AND DATES COVERED
#25

4. TITLE AND SUBTITLE
Studies of the Electrochemical Double Layer at Au(100) in Perchloric Acid Solutions by In Situ Infrared Spectroscopy

5. FUNDING NUMBERS
N00014-93-1-0351

6. AUTHOR(S)
Nebojsa S. Marinkovic, Juan Jose Calvente, Zuzana Kovacova and W. Ronald Fawcett

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
University of California
Davis, CA 95616

8. PERFORMING ORGANIZATION REPORT NUMBER
#25

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Chemistry Division
800 North Quincy Avenue
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Prepared for publication in Journal of the Electrochemical Society

12a. DISTRIBUTION / AVAILABILITY STATEMENT
unclassified

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

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14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| unclassified | unclassified | unclassified | unclassified |

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

revised

# Studies of the Electrochemical Double Layer at Au(100) in Perchloric Acid Solutions by In Situ Infrared Spectroscopy

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ABSTRACT

*In situ* infrared reflection spectroscopy has been used to probe the concentration change of the perchlorate anion in the electrical double layer at Au(100). The results obtained show clearly that there is a correlation between the integrated intensity of the perchlorate band determined in a subtractively normalized interfacial Fourier transform infrared spectroscopic (SNIFTIRS) experiment and the surface excess of the anion in the diffuse layer predicted by the Gouy-Chapman theory. An expression that correlates the above two quantities is derived.

## INTRODUCTION

Studies of the electrochemical double layer using reflectance FTIR spectroscopy date from the work of Pons and Bewick.[1,2] They showed that the accumulation and depletion of ions at a Pt electrode in acetonitrile as a result of electrode potential changes could be followed spectroscopically using a subtractively normalized technique now known as SNIFTIRS.[3] Most experimental work has involved the study of the adsorbed ions which are infrared active such as sulfate,[4] phosphate,[5] and azide.[6] In addition, studies have been directed to the orientation of solvent molecules such as acetonitrile,[7] and dimethylacetamide,[8] at the electrode/solution interface. Several groups have also investigated the potential dependent accumulation or depletion of ions in thin layer electrochemical cells.[9-11] In the present communication, we present results of a study of the change in perchlorate ion concentration in the double layer at a Au(100) single crystal electrode in aqueous $HClO_4$ solutions. The results are compared with the predictions of the Gouy-Chapman theory for the diffuse layer anionic excess in the case that ionic specific adsorption is absent.

## EXPERIMENTAL

The spectroelectrochemical cell was described elsewhere.[7,12] The gold electrodes (Metal Crystals and Oxides, Cambridge, England) with 1 cm in diameter were polished

using standard metallurgical procedures, with a final polishing using 0.05 μm alumina. Before each spectroelectrochemical experiment, the crystal is prepared by extensive cycling between hydrogen and oxygen evolution in 0.01M $HClO_4$. The cleanliness of the solution and the veracity of the crystal structure were checked using cyclic voltammetry. The reference electrode was $Hg/Hg_2Cl_2$ in 0.05M KCl separated from the solution in the cell by a bridge. After obtaining a satisfactory voltammogram, the electrode was pushed against the flat side of the ZnSe hemispherical window until the maximum throughput was achieved.[12] The potential of the working electrode was set alternatively to the sample or reference prior to spectral acquisition. 4096 scans were coadded, in 32 cycles with 128 scans each; 4 $cm^{-1}$ resolution and parallel polarized light were selected in all measurements. The reference potential was constant and set just before the onset of oxide formation, while the sample potential was changed by 0.1 V starting from the most positive potential and going in the negative direction, so as to cover eventually the whole double layer region.

## RESULTS AND DISCUSSION

The SNIFTIR spectra for Au(100) in 0.1 M and 1 M $HClO_4$ are shown in Figure 1. The common feature is a strong negative-going band centered at 1109 $cm^{-1}$. The negative direction of the band is the consequence of the choice of the sample and reference potentials. The concentration of perchlorate is high in the diffuse double layer at the reference potential, and smaller at sample potentials, so that the normalized difference

in the infrared spectral intensities produces a negative going band. It should be pointed out that all the IR features that are common in both intensities at the reference and the sample potentials cancel out. Therefore, since the only difference between the spectra at the two potentials is the perchlorate concentration change, it can be inferred that the SNIFTIRS can be used to determine the surface excess of perchlorate ion in the double layer, and, if the ion is not adsorbed, to test the Gouy-Chapman model. Furthermore, such a test can be extended to higher concentrations where double layer properties are more difficult to study electrochemically.

Figure 2 shows a cyclic voltammogram of the double layer region of Au(100) in 0.1 M and 1 M $HClO_4$, together with the integrated intensities $A_{\Delta R/R}$ of the perchlorate band. In order to understand the dependence of $A_{\Delta R/R}$ on potential it is necessary to determine the location of the potential of zero charge, $E_z$. In the absence of ionic specific adsorption the potential of zero charge is given by the minimum (in absolute value) on the current - potential curve. This is a consequence of the contribution of the diffuse part of the double layer to the interfacial capacity. As can be seen, the minimum is clearly observed for a bulk solution concentration of 0.1 M, at $E_z = -0.15$ V, but scarcely visible at the higher concentration. The latter observation results from a decrease of the effect of the diffuse layer on the interfacial capacity as the ionic strength increases. One of the aims of this study is to explore whether the SNIFTIRS technique can be used to confirm the location of the $E_z$ even in concentrated solutions, where conventional electrochemical techniques are not applicable.

The potential behavior of the integrated band in Figure 2 is consistent with the prediction that the negatively charged $ClO_4^-$ ions leave the double layer as the potential becomes more negative. The absolute value of the integrated band intensity increases as the potential is made more negative as a consequence of the concentration change between the two potentials, which also increases in value. As the potential approaches $E_z$, the diffuse layer is relatively depleted of anions and, according to the Gouy-Chapman model, the concentration difference should reach a limiting value. As Figure 2 shows, the value of $A_{\Delta R/R}$ also reaches a limit. It should be noted that the integrated band intensities for the two concentrations show the same trend, reaching a limiting value close to the point of zero charge (pzc). This can be interpreted as an indication of the absence of specific adsorption in this potential region.

The integrated band intensity is proportional to the change in the concentration between the sample and the reference potentials, so that:

$$A_{\Delta R/R} = -K \frac{c_- - (c_-)_r}{(c_-)_r} \qquad (1)$$

where K is a constant related to the extinction coefficient and $c_-$ and $(c_-)_r$ are the effective concentrations of $ClO_4^-$ at the sample and reference potential, respectively. The minus sign is inserted to ensure that the positive going bands present the gain of a particular species at the sample potential relative to that at the reference. In the absence of specific adsorption the difference $c_- - (c_-)_r$ can be expressed in terms of the difference of the anionic charge in the double layer between the two potentials. This is true because the

contribution from the bulk of the solution is canceled out.[13] Therefore, eq. (1) can be transformed to:

$$A_{\Delta R/R} = D\,[\sigma_{-} - (\sigma_{-})_r\,] \qquad (2)$$

where $\sigma_{-}$ is the anionic surface excess at the sample potential, $(\sigma_{-})_r$, the value at the reference potential, and D includes the concentration at the reference potential and parameters related to the absorptivity.

In the absence of specific adsorption, at the pzc $\sigma_{-} = 0$. Inserting the above condition in eq. (2), it is found that:

$$D = -\,(A_{\Delta R/R})_z \,/\, (\sigma_{-})_r \qquad (3)$$

where $(A_{\Delta R/R})_z$ is the value of $A_{\Delta R/R}$ at the pzc. Then equation (2) may be written as

$$A_{\Delta R/R} = (A_{\Delta R/R})_z + D\sigma_{-} \qquad (4)$$

Another way of expressing the absorption data is in terms of a normalized intensity difference defined as

$$A^{*}_{\Delta R/R} = \frac{[A_{\Delta R/R} - (A_{\Delta R/R})_z]}{D} = -\sigma_{-} \qquad (5)$$

Using this parameter results from different experiments involving varying $ClO_4^-$ concentrations can be compared. Equation (5) is a phenomenological expression for the dependence of the normalized integrated intensity due to the anion on its charge in the

double layer provided only one type of species contributes to the observed absorption. This normally means that the anion not be contact adsorbed on the electrode, because such a species might be expected to have a different extinction coefficient than the same anion in the diffuse part of the double layer.

From the cyclic voltammogram one estimates $E_z$; the electrode charge density is calculated by integrating the capacity from the potential of zero charge to the potential of interest; the charge in the diffuse layer is then calculated by applying the Gouy-Chapman equations.[14] From the $A_{\Delta R/R}$ against E curve, one estimates $(A_{\Delta R/R})_z$ as the specific value of the integrated intensity at the pzc. Values of D were determined for each experiment from a plot of $A_{\Delta R/R}$ against $\sigma_{-}^{GC}$ in the vicinity of the pzc. Data obtained for 0.1 and 1 M aqueous solutions of $HClO_4$ are shown in terms of the normalized intensity difference in Figure 3. The straight line was drawn with unit slope. Obviously, there is excellent agreement between experiment and theory in the region $|\sigma_{-}^{GC}| < 10\ \mu C\ cm^{-2}$. For values of $\sigma_{-}^{GC}$ more negative than $10\ \mu C\ cm^{-2}$, deviation from the values expected by the Gouy-Chapman model is observed at both $HClO_4$ concentrations. This can be explained as being due either to anion specific adsorption. or to failure of the Gouy-Chapman model at higher positive electrode charge densities.

In conclusion, the results presented clearly show that SNIFTIRS is an powerful tool for quantitatively investigating the electrochemical double layer. In the absence of specific adsorption it can be used to follow the concentration changes in the double layer and to compare the results with the predictions of the model used to estimate the surface excess. In order to check the validity of the above approach further, the present study is

being extended to other crystallographic orientations of gold, and will be presented in a future paper.

ACKNOWLEDGMENT

The financial support of the Office of Naval Research, Washington is gratefully acknowledged. J.J.Calvente thanks the Ministerio de Educacion y Ciencia, Spain, for an FPI fellowship held at UC Davis.

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FIGURE CAPTIONS:

Figure 1. SNIFTIR spectra of the perchlorate band due to the double layer at a Au(100) electrode. Electrolyte solution concentration 0.1 (a) and 1 M $HClO_4$ (b). Reference potential is held constant at 0.69 V and the sample potentials are decreased in 100 mV increments, starting from 0.39 V (top spectrum). 4096 scans with *p* polarized light and 4 $cm^{-1}$ resolution are coadded.

Figure 2. (a) Cyclic voltammetry of the Au(100) electrode in the double layer region for the 0.1 M (———) and 1 M (· · · · ·) bulk solution concentration of perchloric acid, (b) integrated area of the perchlorate band $A_{\Delta R/R}$, obtained in 0.1 M (O) and 1 M $HClO_4$ (Δ).

Figure 3. Comparison of the predicted values of the normalized intensity difference on the basis of equation (5) with the anionic charge in the diffuse layer calculated by the Gouy-Champan model, for 0.1 M (O) and 1 M (Δ) $HClO_4$.

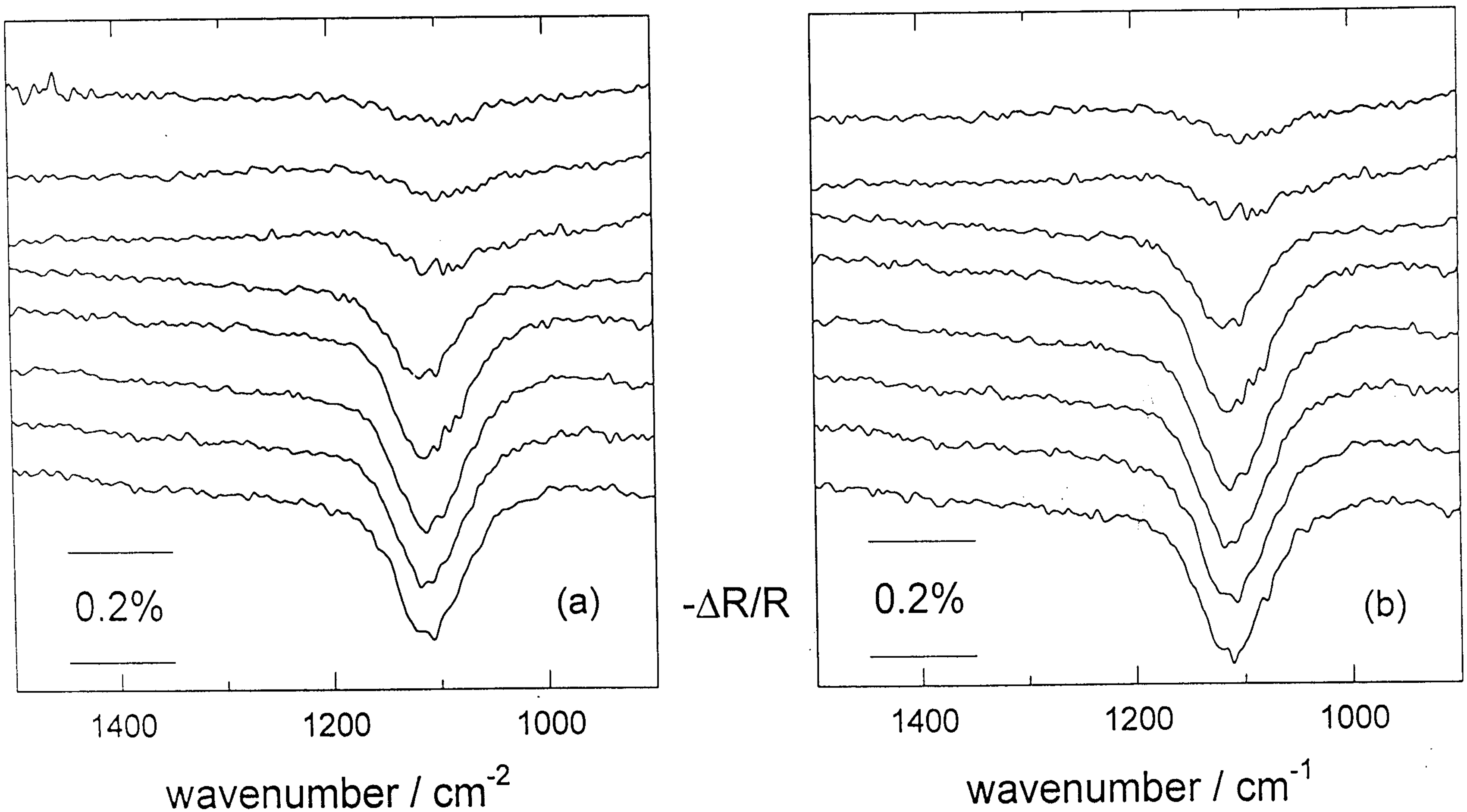
0.2%
(a)
1400
1200
1000
wavenumber / cm$^{-2}$
-ΔR/R
0.2%
(b)
1400
1200
1000
wavenumber / cm$^{-1}$

Figure 1

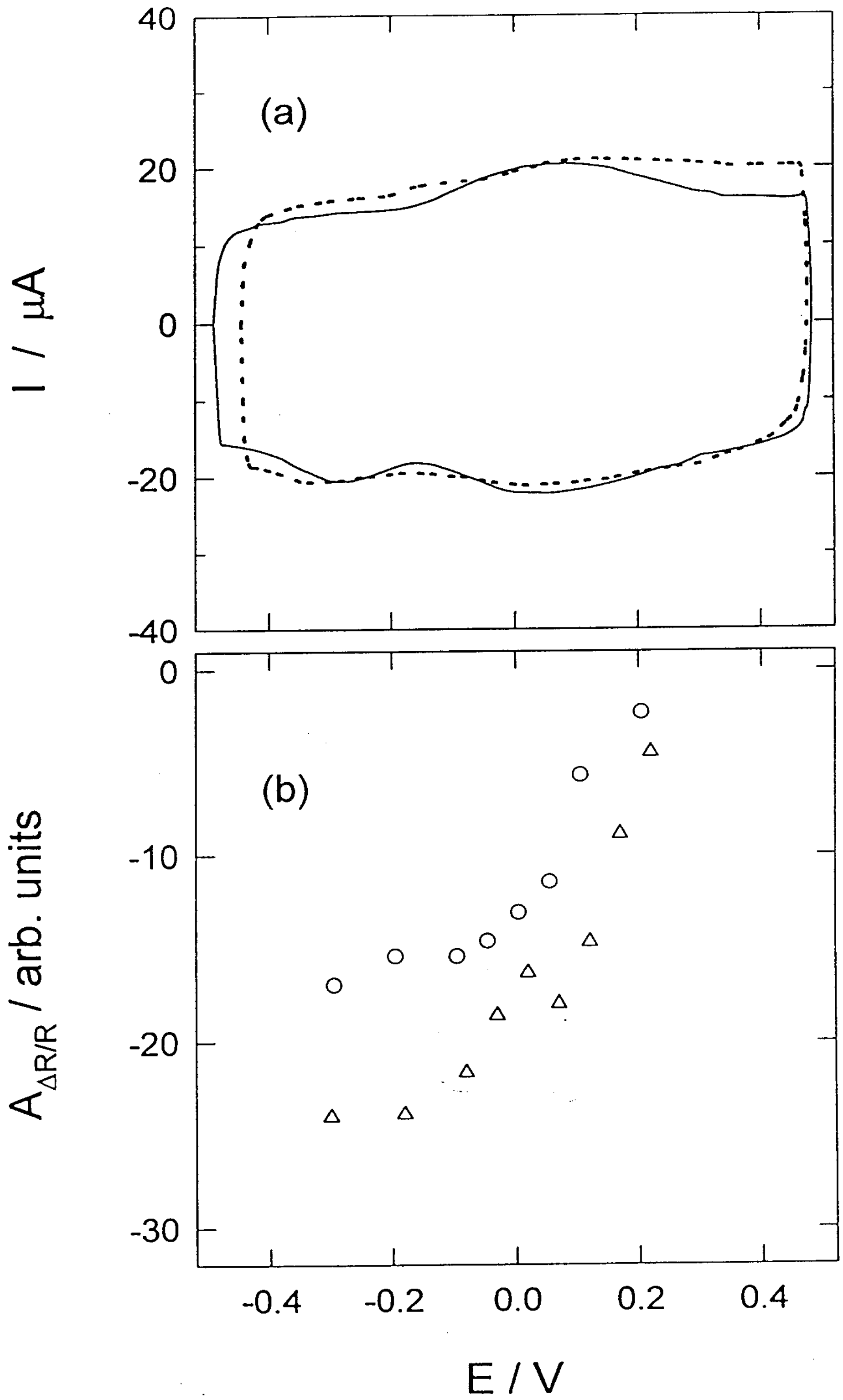


Figure 2

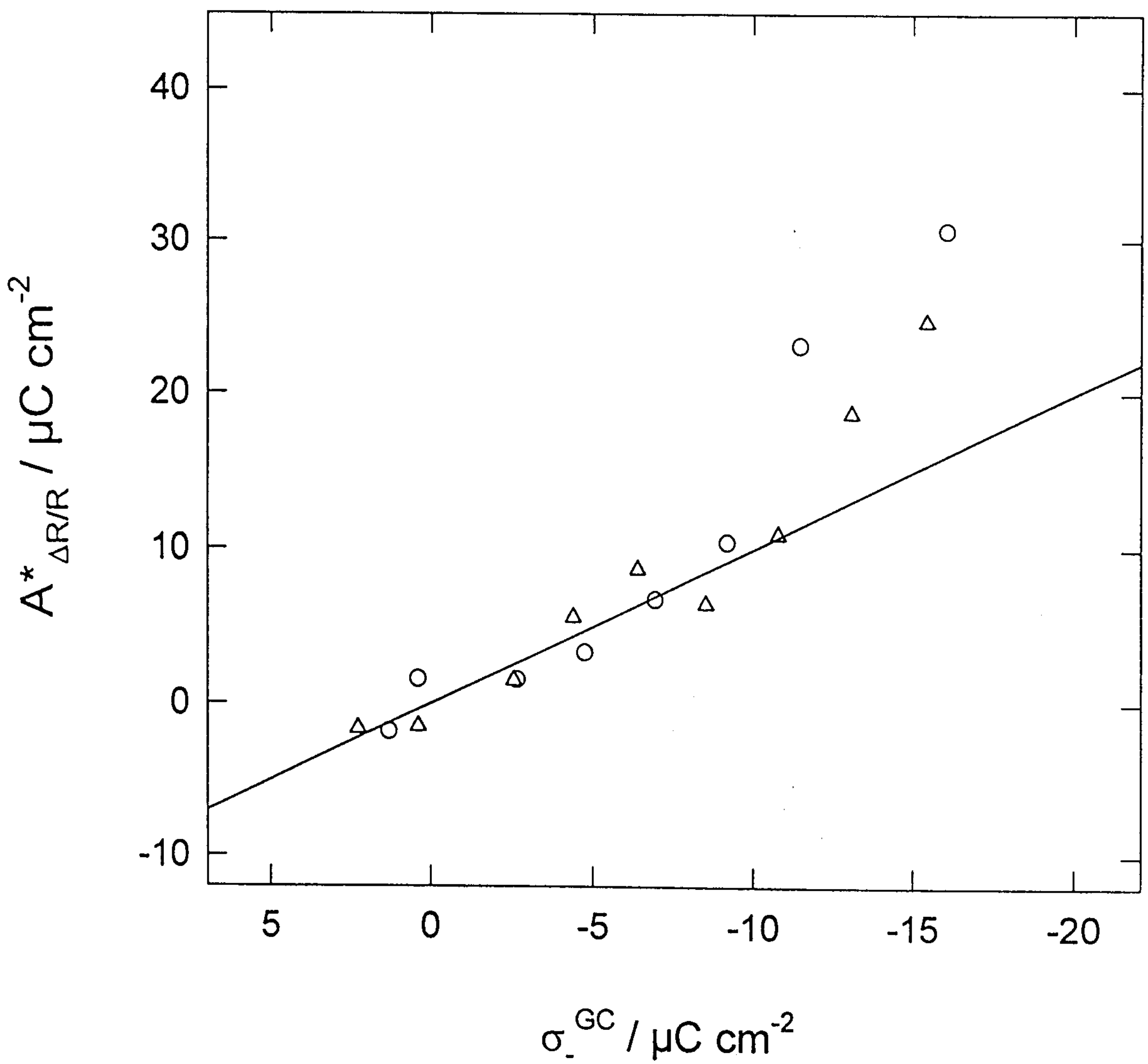


Figure 3